Pipeline Corrosion R&D at NIST

Richard E. Ricker

Metallurgy Division
Materials Performance Group
Materials Science and Engineering Laboratory
National Institute of Standards and Technology
US Dept. of Commerce, Tech. Admin.
Gaithersburg, MD 20899-8553
richard.ricker@nist.gov

NIST Pipeline Research

Two Program Areas

Corrosion

1. R. E. Ricker
2. D. Pitchure
3. U. Bertocci (ret)
4. H. Gates (pt)

Fatigue and Fracture

1. T. Siewert
2. D. McColskey
3. C. McCowan
4. P. Darcis
5. R. J. Fields (ret-cont)
6. S. Mates

NIST Pipeline Activities

NIST and OPS Collaborate in Variety of Activities

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1. Government-Industry R&D Forums
2. Hosted 2 OPS-Industry R&D Workshops (Coatings & Welding)
3. Prepared and published proceedings of 2 workshops
4. Participation on R&D Program Review Panel
5. Participation on PSIA Coordination Council
6. Participation in PL SDO Coordination Council
7. Participation on proposal review panels
8. Participation in PL conferences etc.

NIST Pipeline Corrosion Research

Two Distinctly Different Phases of the Program

Phase 1: Reexamination and Analysis of Data from the Original NBS (NIST) Pipeline Underground Burial Studies Conducted from 1922 to 1957

Phase 2: Laboratory Studies to Evaluate Hypotheses Developed During Phase 1 Relevant to Prediction of Expected Corrosion Rates From Laboratory Measurements and the Development of Corrosion Hazard Dependent Inspection Intervals

NIST Pipeline Corrosion Research

Different Phases and Objectives, but Same Goal

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The ultimate goal of both phases is essentially the same: to determine if a more sound basis can be developed for determining, or adjusting, inspection intervals.

For example, the inspection interval (t_{insp}) would be determined from the expected minimum time to penetration ($\langle t_{MP} \rangle$) as

$$t_{insp} = k_{SF} \langle t_{MP} \rangle$$

where k_{SF} is an engineering safety factor based on NDE, fracture mechanics, etc.

The difference in the phases is the approach to estimating the expected minimum time to penetration

Phase 1: $$\langle t_{MP} \rangle_I = f(Envir, FieldData, etc.)$$

Phase 2: $$\langle t_{MP} \rangle_{II} = f(Envir, LabMeas, etc.)$$

NIST Pipeline Corrosion Research

Time to Failure Estimation

The time for the failure can be approximated as the sum

$$t_f = t_f(coating) + t_d(CP) + t_p(Bare) + \ldots$$

Since the time for the coating system to fail and the time delay due to cathodic protection, t_d(CP), will be >0, estimating them and any other terms as 0 is a conservative estimate

$$t_f \cong t_p(Bare)$$

This is why the "bare pipe" corrosion rate is relevant

The expected minimum time to penetration is then

$$\langle t_{MP} \rangle = \Delta h / P^* = \Delta h / (Z_P R)$$

Where P* is the maximum expected corrosion penetration rate, Δh is the critical change in flaw size, Z_P represents probability distribution terms, and R is the average corrosion rate.

Put simply, the objective is to identify a reliable estimation technique for P* or R.

Phase 1 - Objectives

Starting with the results of original NBS burial studies for bare pipe in different soils;

(1) Analyze the data (new look, techniques, angles)

(2) Look for previously unrevealed relationships (new meaning)

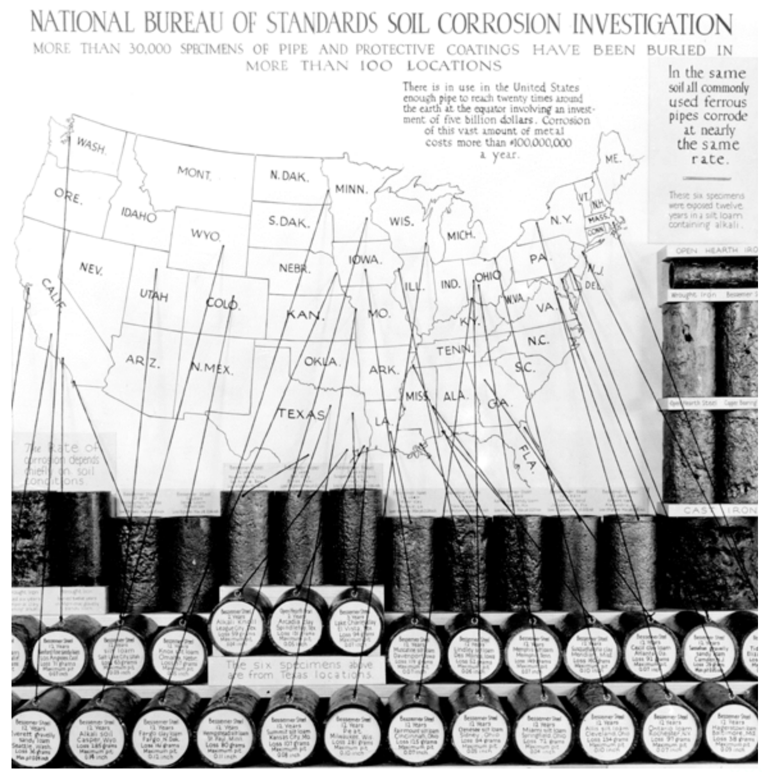
(3) Identify R&D needs (gap analysis)

(4) Identify a path forward (experiments)

(5) Create understanding (results)

(6) Implement change (impact)

Why? - Industry



Objective:

Review NBS Underground corrosion studies 1910-1957

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Phases of Program

1. **1910: Congress authorized stray current corrosion study**
2. **1920: Workshop convened to plan an underground corrosion study**
   - **a) Dept of Agriculture selects sites**
   - **b) Industry identifies and provide materials**
   - **c) Symposia held every 5 years**
4. **1922: Ferrous pipe materials at 47 sites for 12 to 17 years**
5. **1924: Other materials buried at the sites during first retrieval**
6. **1928: Fe alloys, Cu, Cu alloys, and Pb samples buried at new sites**
6. **1932: Materials for corrosive soils study using 15 sites (coatings)**
7. **1937, 1941, 1947 materials added during retrievals at the 15 sites**
8. **1945: "Underground Corrosion" by K. H. Logan NBS C450**
9. **1952: Last retrival - 128 sites, >36,000 samples, 333 matl types**
10. **1957: Final Rpt. "Underground Corrosion" by M. Romanoff NBS C589**
11. **A larger number of follow-on studies from 1957 to the present:**

Ductile Cast Iron, Concentric Neutrals, Steel Pilings, Offshore Pilings, Stainless Steels (buried 1970s), Bridge Deck Corrosion, etc.

Conclusions of Old NBS Studies

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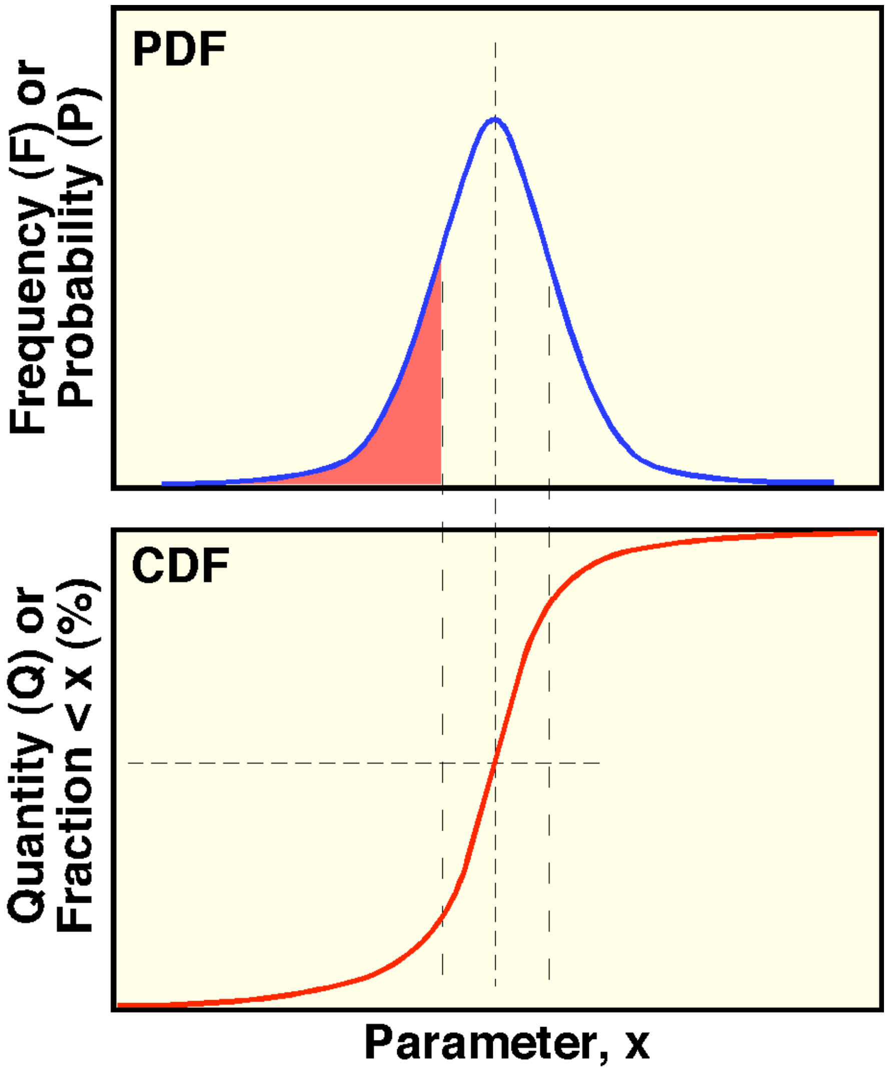
1. Some soils are very corrosive to bare pipe
2. Some soils are not very corrosive to bare pipe
3. Localized attack (pitting) is a problem in some soils
4. Large scatter was observed and attributed to variability of conditions
5. All ferrous materials corroded at about the same rates (well within the measurement scatter)
6. Considerably less corrosion was observed in piles driven into undisturbed soil than in this study with disturbed (aerated) soils.
7. Clearly three factors stand out:
    1. Aeration (disturbed vs. undisturbed),
    2. Drainage (water in contact with surface),
    3. High statistical variation in local occlusion cells
    4. Conductivity indicates total salt content, and
    5. Conductivity is only a rough indicator of soil corrosivity.

Statistical Analysis of Scatter

Different Ways to Graph the Same Distribution



Probability Density Function (PDF)
Represents the frequency or probability of each value of "x" occurring.

Cumulative Dist. Function (CDF)
Represents the probability "x" occurring between -∞ and "x"

$$CDF(x) = \int_{-\infty}^{x} PDF(x)dx$$

NBS Underground Test Data

Taking All Sites and Alloys Together

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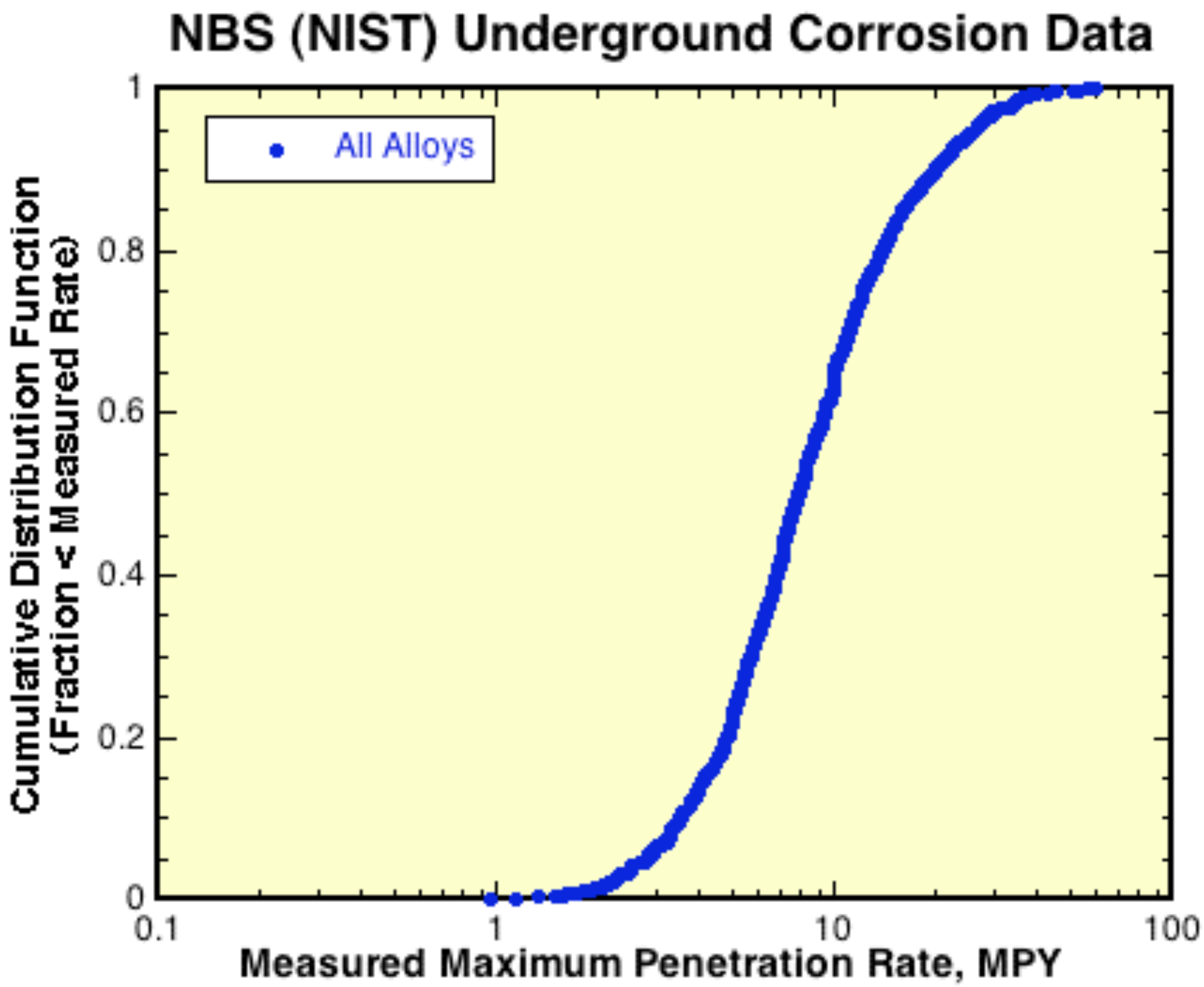

***Average of the maximum penetration measured on two samples.**

NBS Underground Test Data

Alloy Composition Effect

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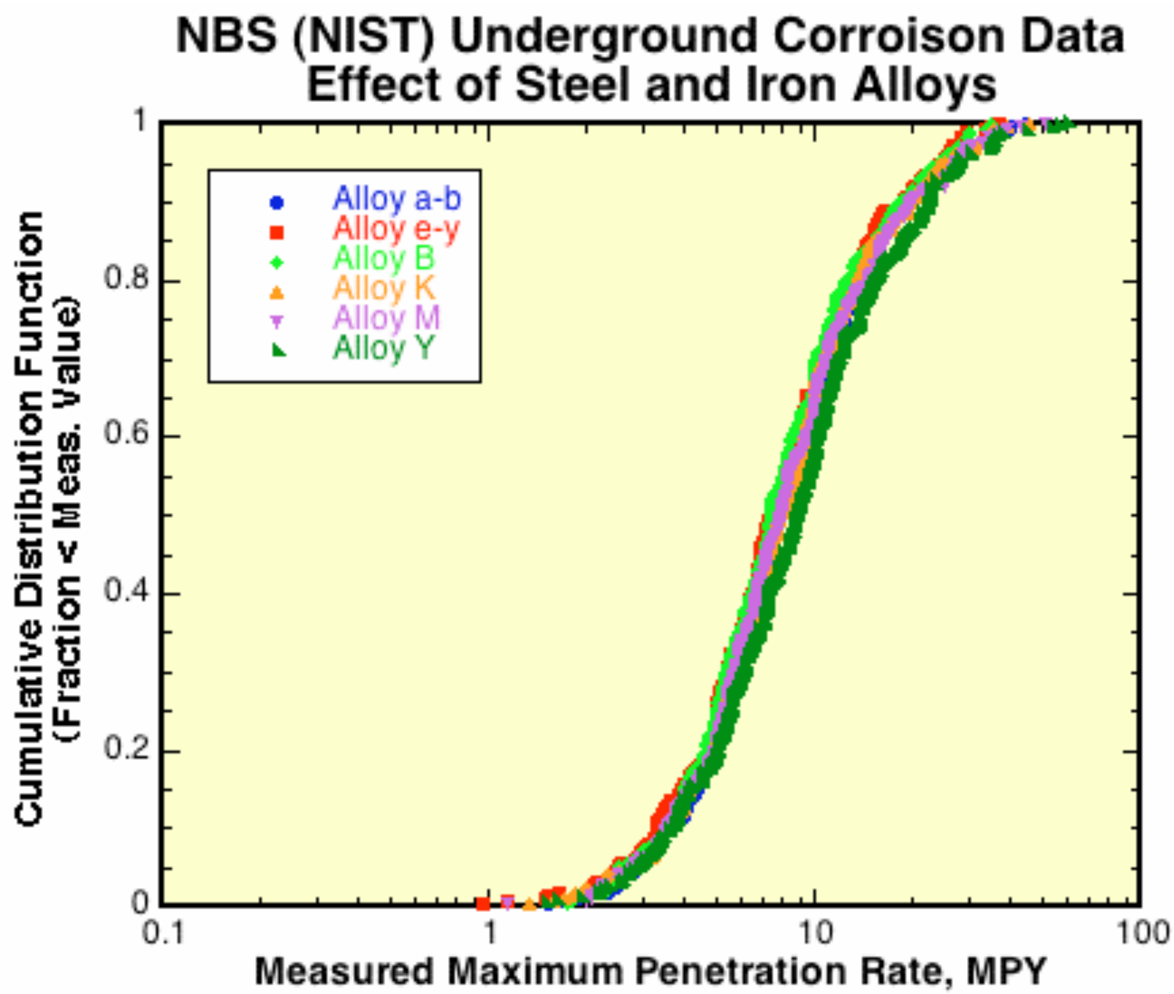
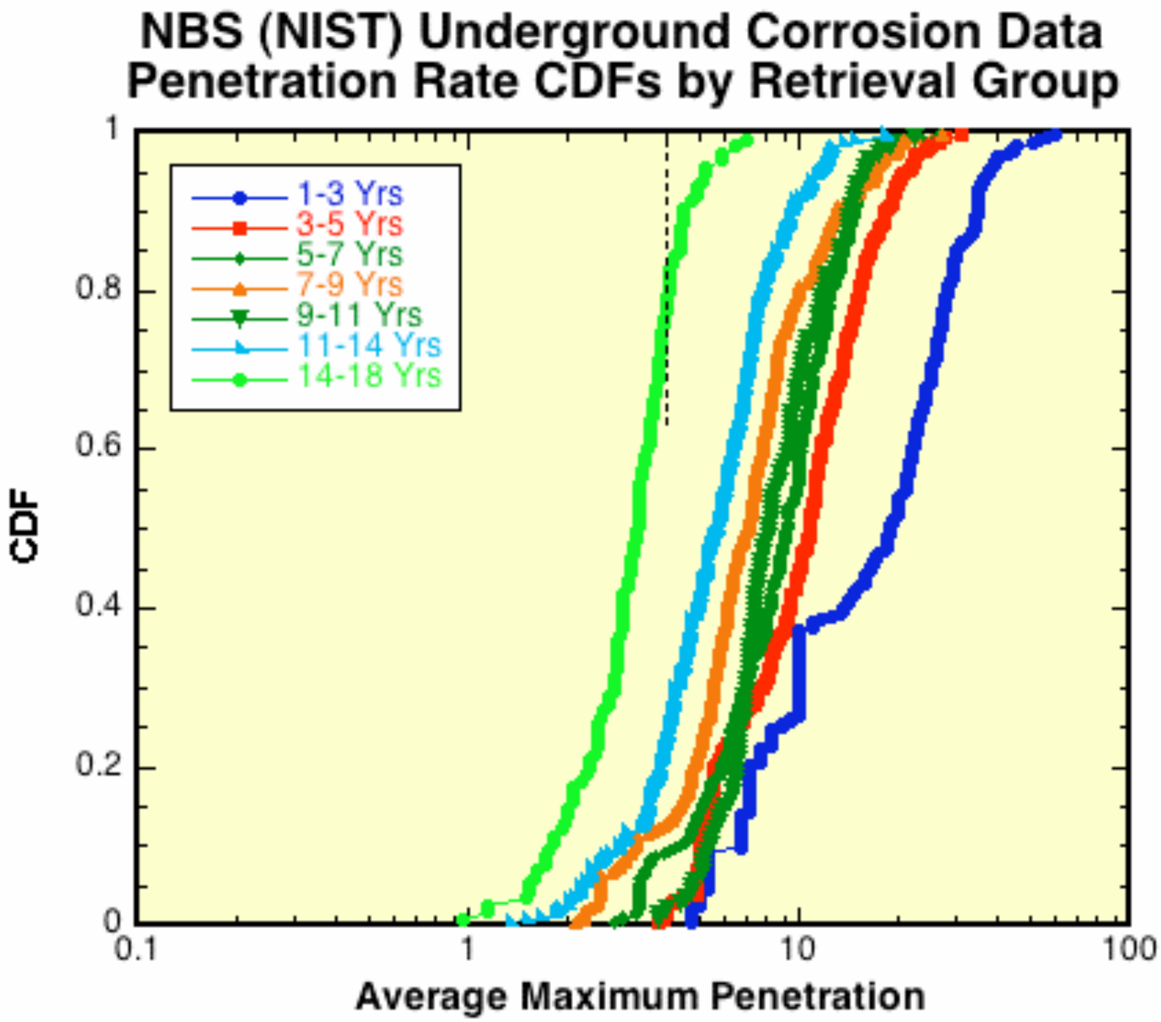


Almost no effect of alloy composition compared to other sources of scatter

NBS Underground Test Data

Sorting by Retrieval Group Showed a Trend



The average growth rate and its range diminished with exposure time.

Kinetic Analysis

Bare surface with mixing

$$P=kt$$

Surface film slows transport

$$P=kt^n \qquad n=1/2,\ 1/3,\ 1/4$$

Reactant consumed from environment

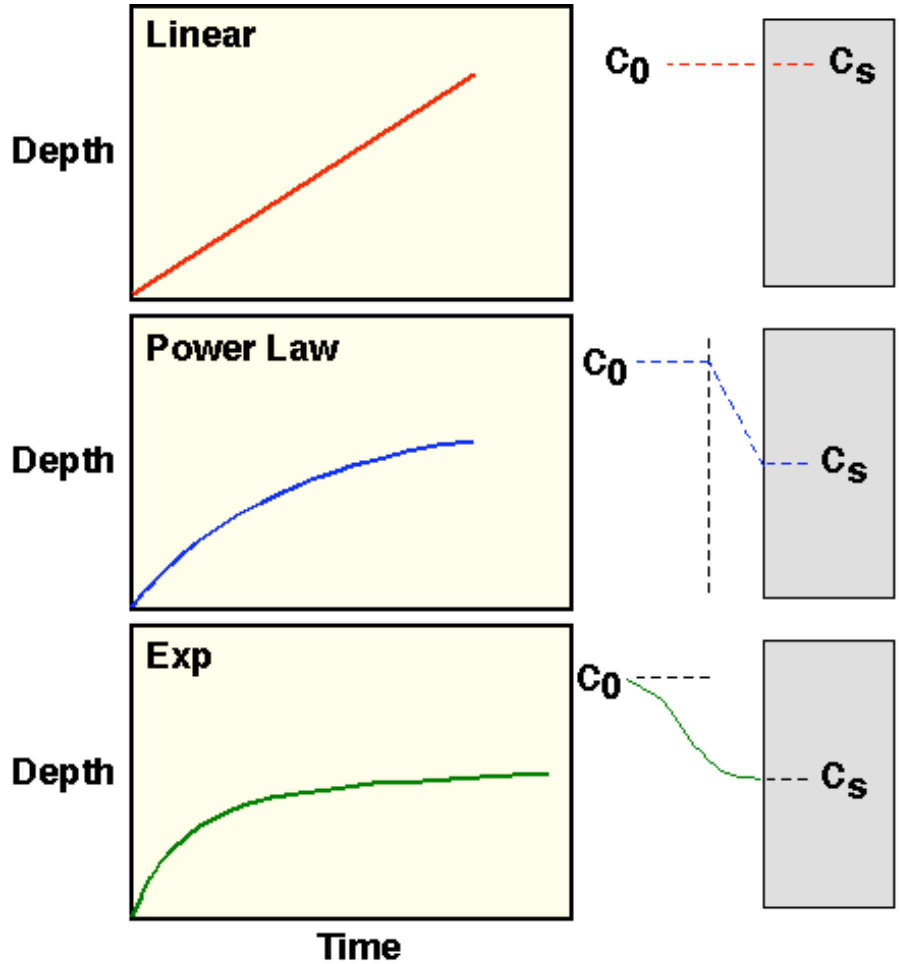
$$P=k[1-\exp(-t/b)]$$

Therefore, the slope n is an indicator of the rate determining (limiting) process

Two rates:

- **(i) corrosion rate, and**
- **(ii) the penetration (pitting) rate**

The pitting factor (PF) is the ratio of these two rates



Original Analysis
Analysis of Corrosion Kinetics

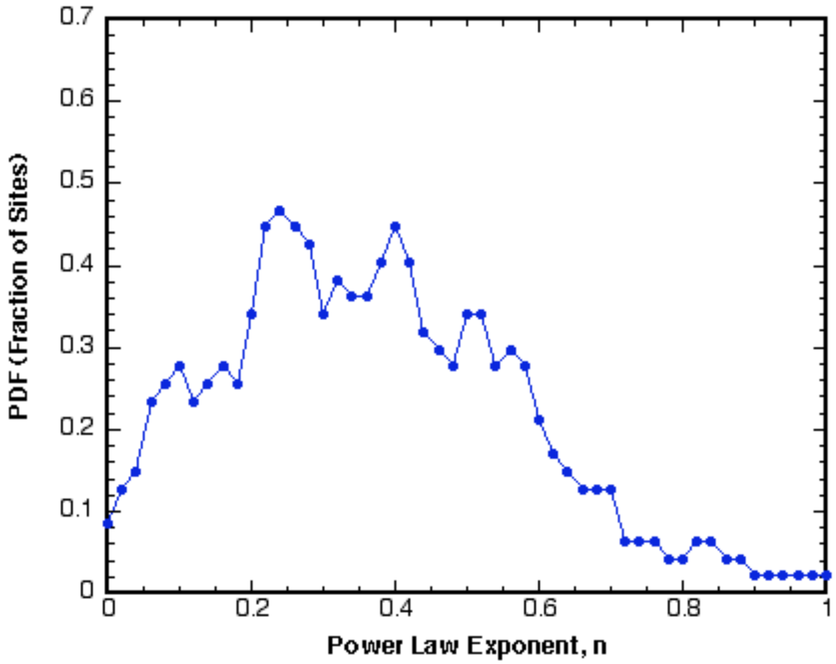
Regression analysis for relationship of the form

$$D=kt^n$$

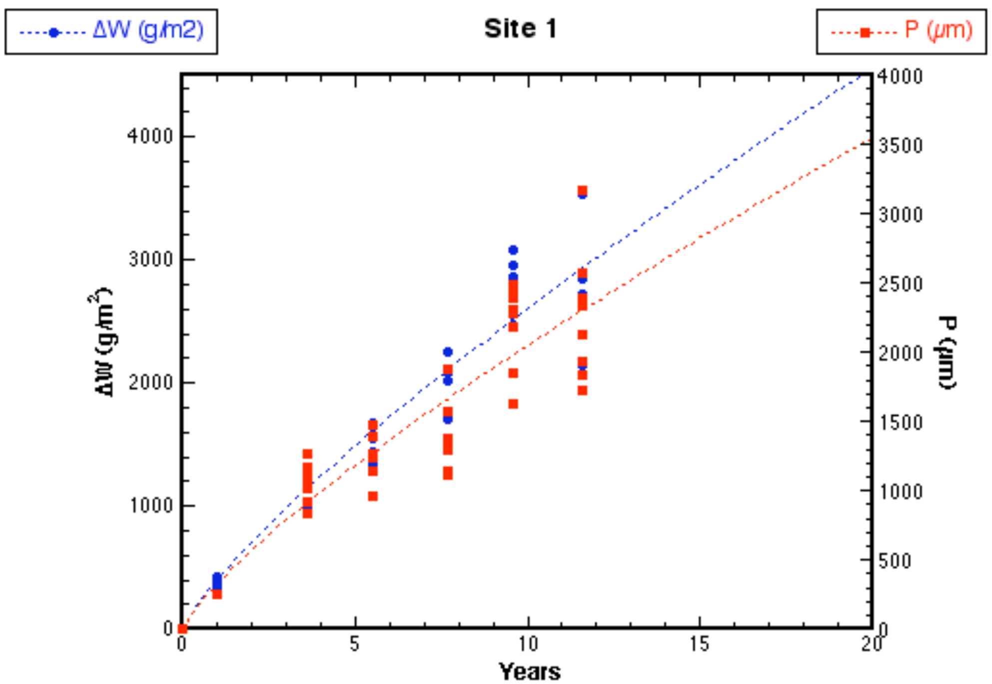
The original NBS analysis determined an average k and n for each of the 47 soils. These were determine by linear regression of the equation

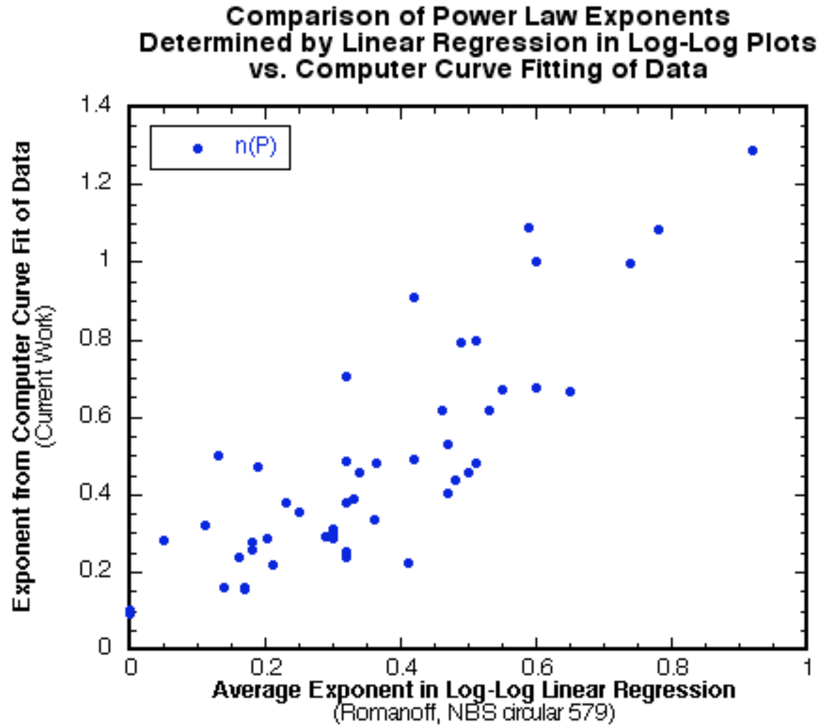
$$\text{Log (D)} = \text{Log (k)} + n \text{ Log (t)}$$

Multiple linear regression of the k and n values as a function of soil properties met with only moderate success



Reevaluation of Individual Site Data





Mass Loss

y = a*x^b		
	Value	Error
a	403.31	40.788
b	0.80955	0.046171
Chisq	2.9037e+06	NA
R	0.97535	NA

Penetration

y = a*x^b		
	Value	Error
a	328.16	49.903
b	0.79454	0.069531
Chisq	4.1868e+06	NA
R	0.94491	NA

Comparison of Exponent Distributions

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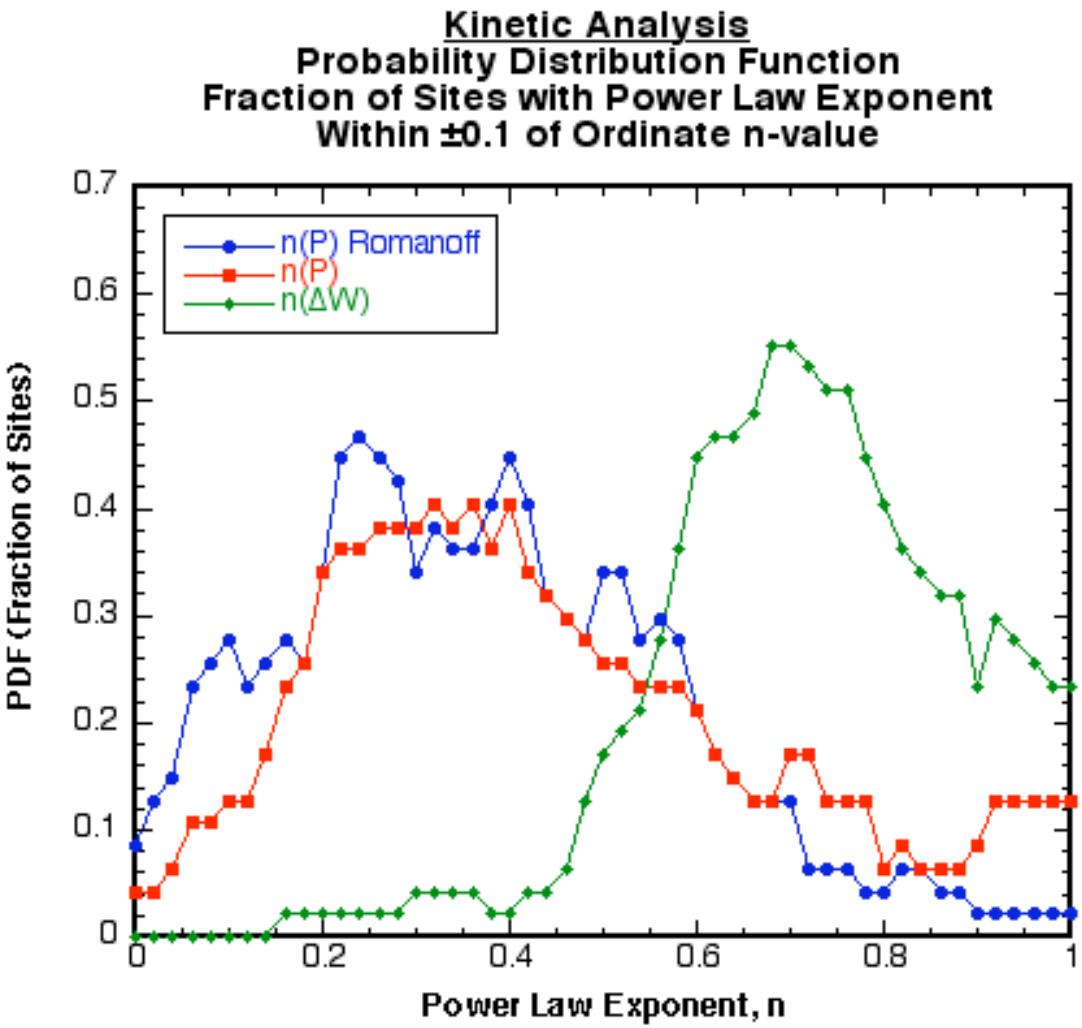
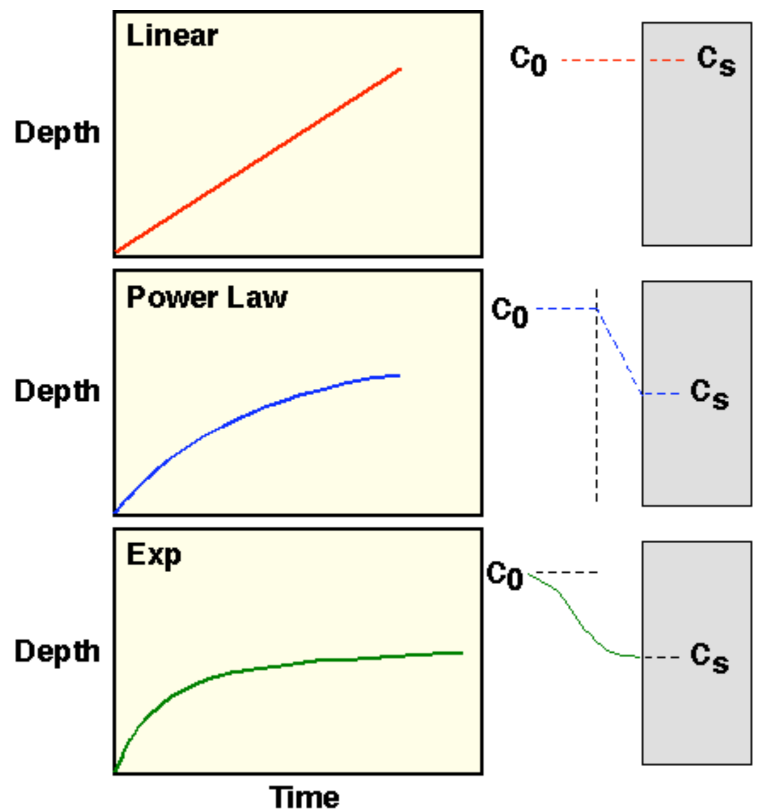




Results of Kinetic Analysis

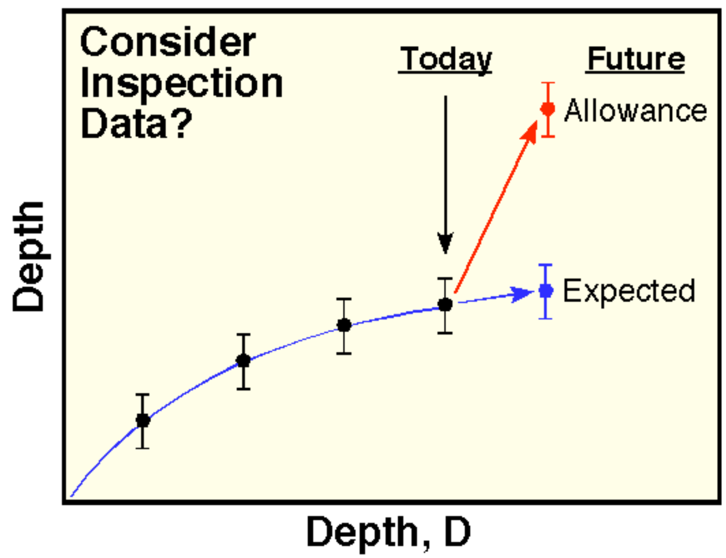
(1) **Analysis of the maximum pit depth data indicates that pits grow at a rate that decreases with exposure time.**

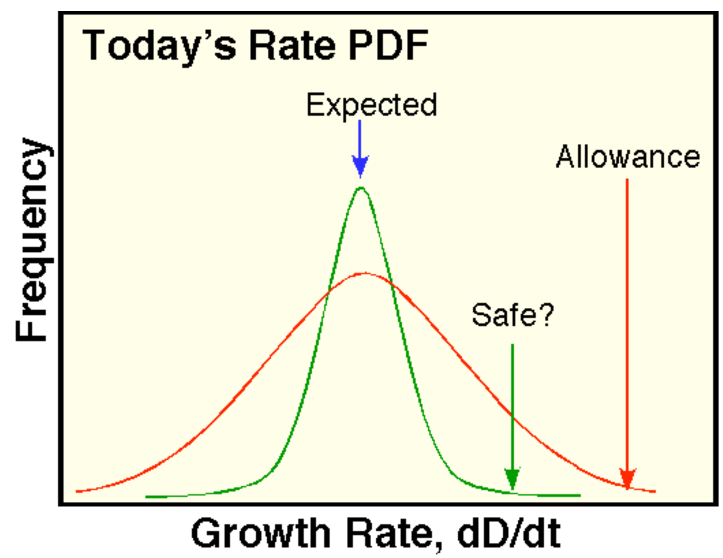
(2) **For maximum pit depths, the exponent varied from about 1/4 to 1/2.**

(3) **Analysis of the mass lost data indicates a higher exponent or mixed rate determining kinetics (e.g. pitting and uniform attack)**

(4) **Multiple regression analysis for environmental factors influencing the exponent n has not yielded any significant environmental indicators.**

(5) **Understanding the origin of the scatter in the data should help analysis.**

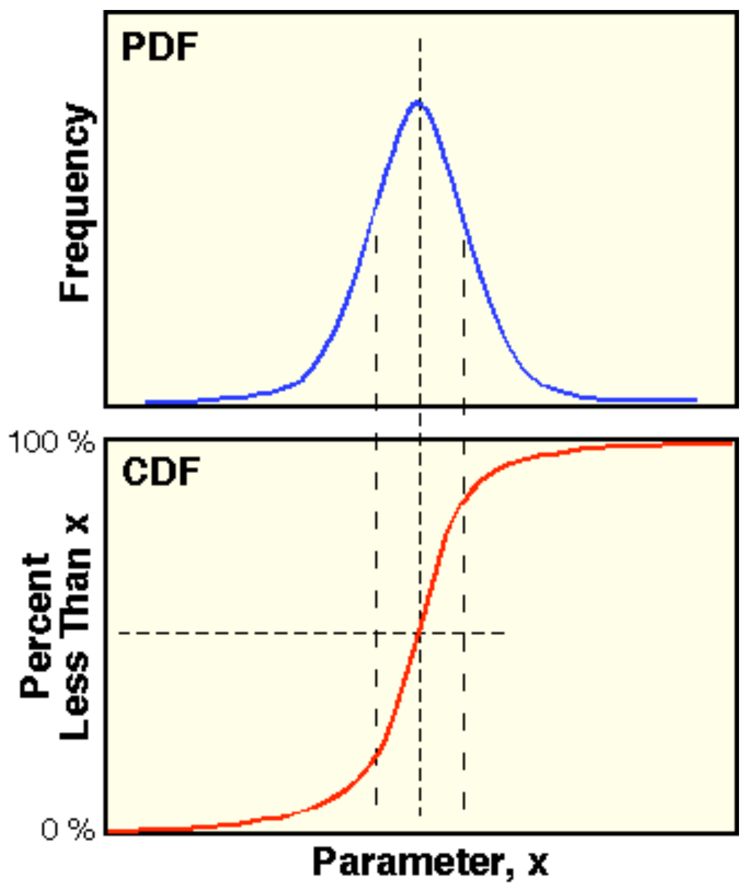




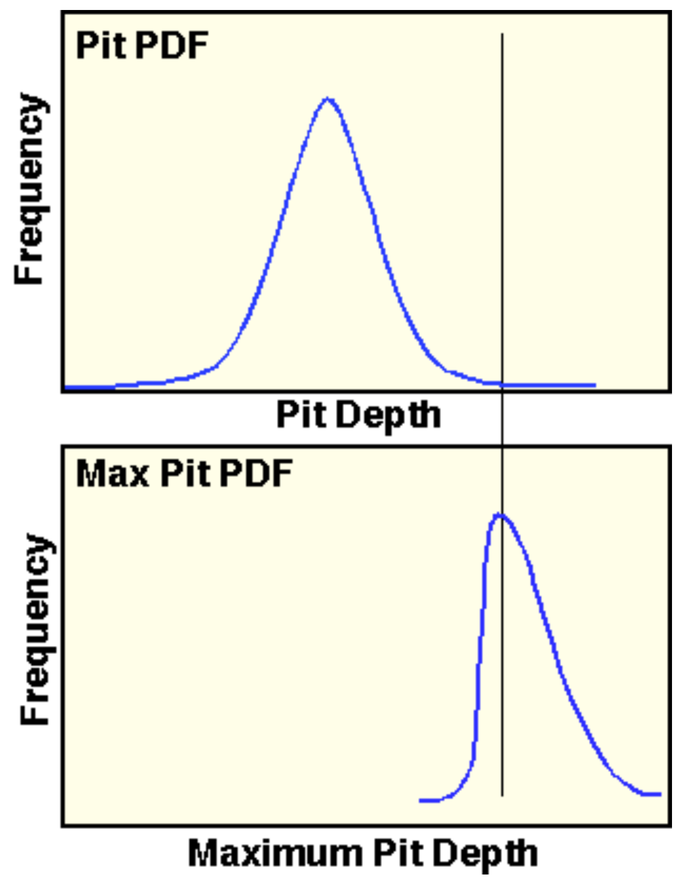
Statistical Analysis of Scatter

Extreme Value Statistics

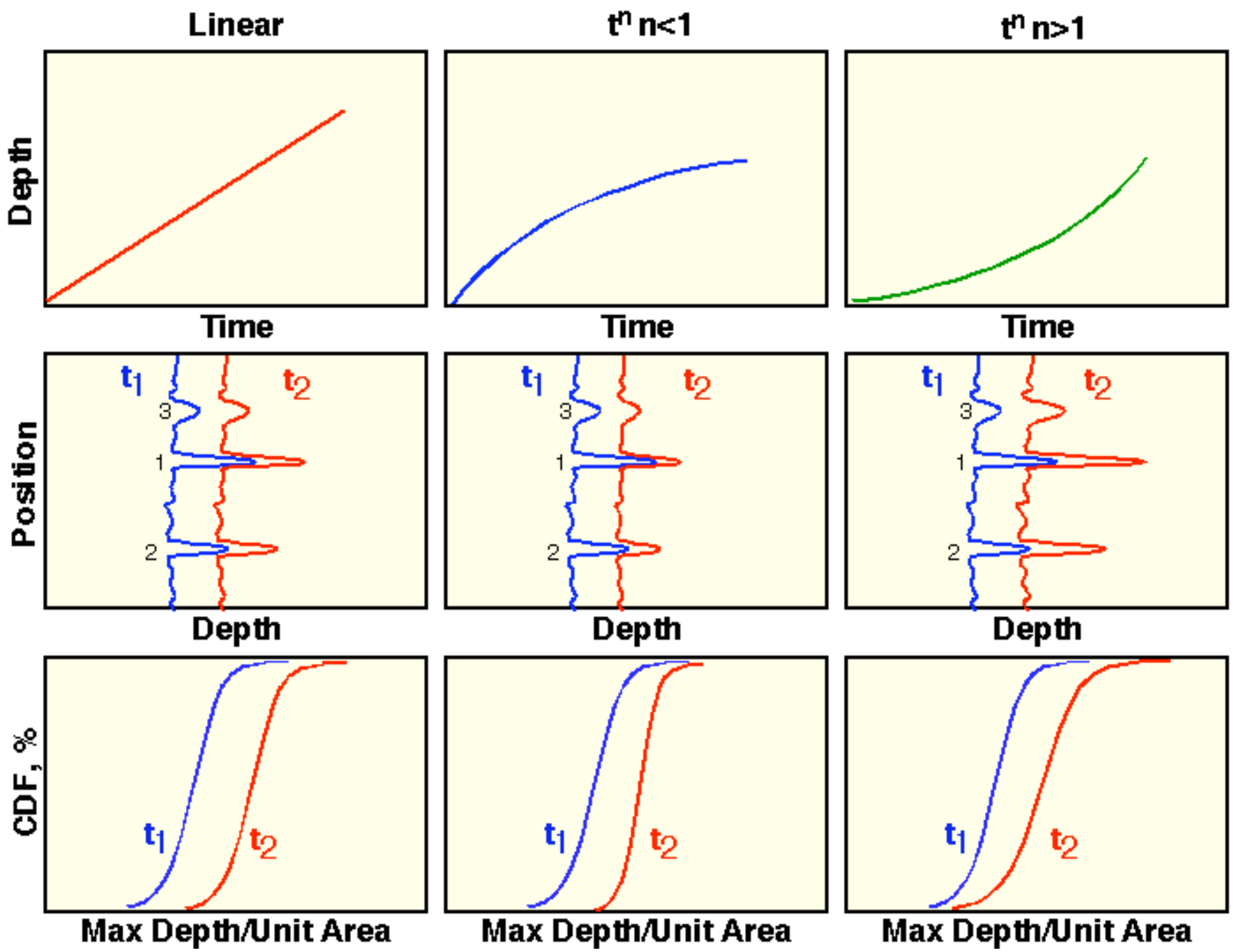
Fundamental Distributions



Fundamental and Extreme Value Distributions

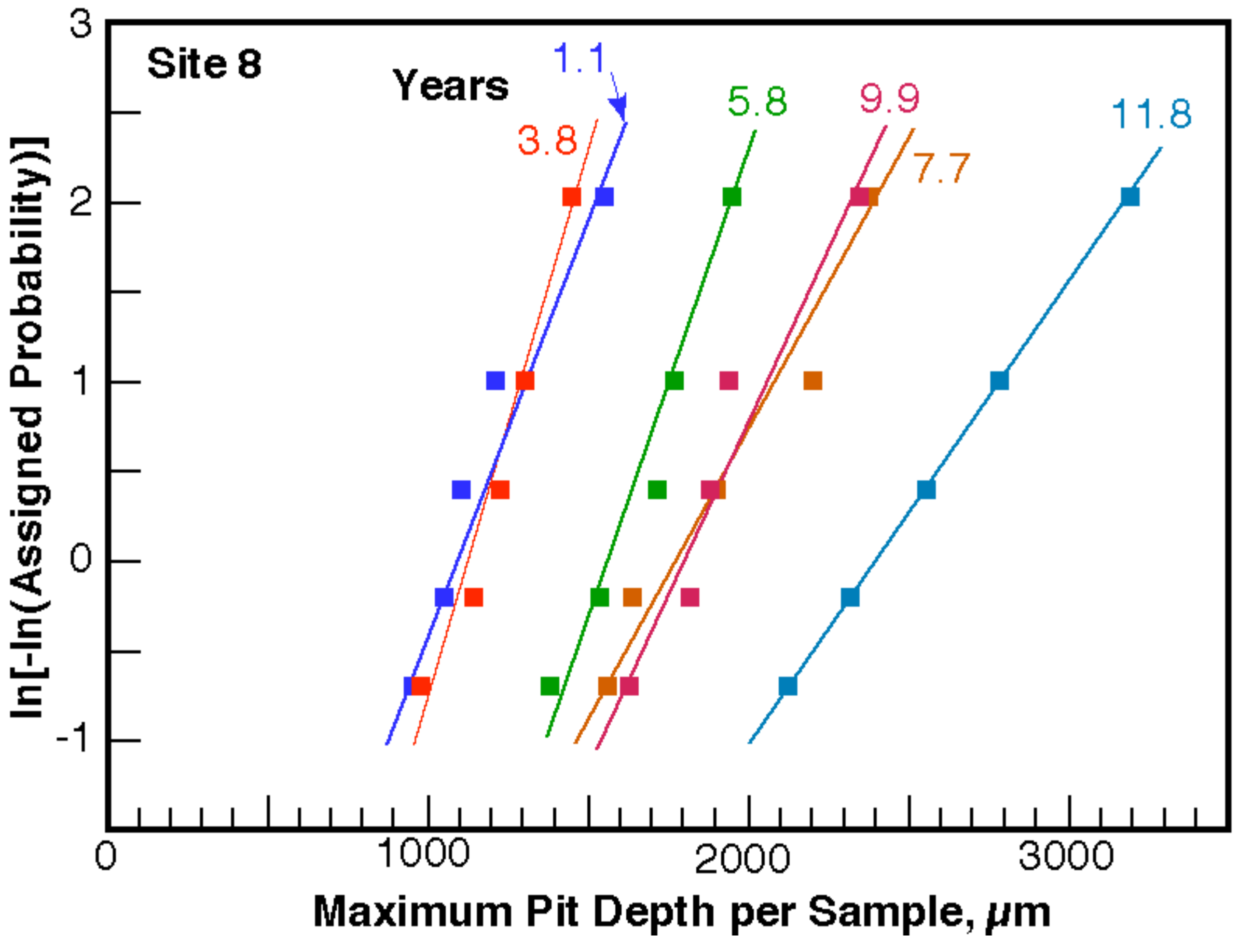


Kinetic Models and Scatter



Note, one assumes that the initial scatter is due to initiation times

Example Site Data

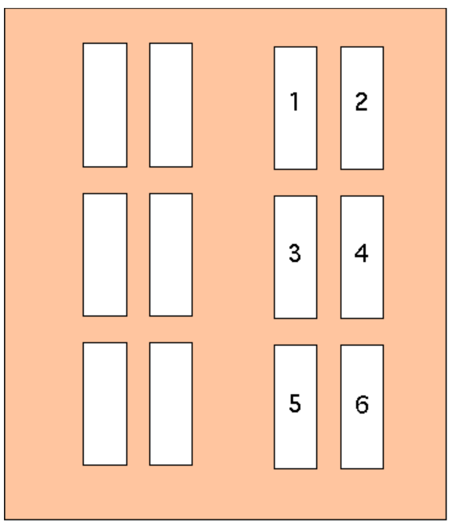


Evidence for constant, increasing, and decreasing slopes were observed

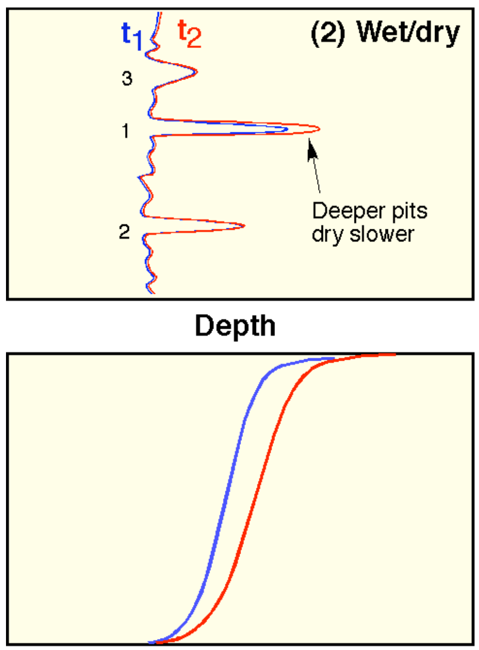
Results of Extreme Value Analysis

- Scatter consistent with different kinetic models were observed.
- This may not be inconsistent with a decreasing rate model
- The source of the scatter needs to be understood.
    1) Variation in the environment
    2) Alternating wet and dry
    3) Salts in pit absorbing water

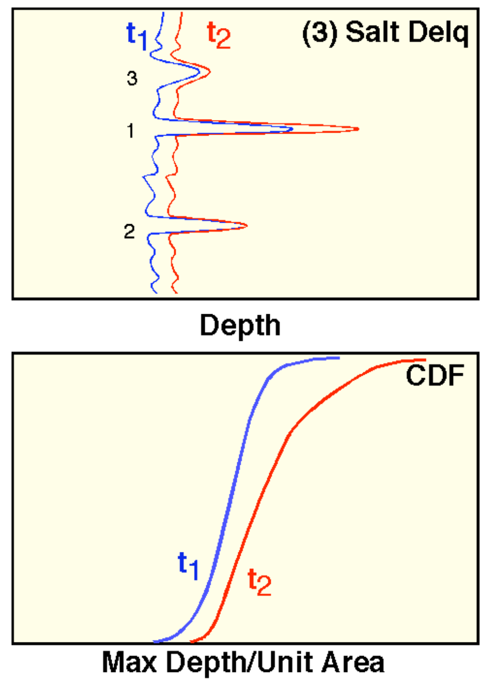
Hypothesis 1



Hypothesis 2



Hypothesis 3



Phase 2 - Objectives

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(1) Try to identify the major source of scatter (develop hypotheses)
(2) Develop an experimental method for testing hypotheses
(3) Develop a scheme for modeling influence of scatter source
(4) Evaluate postulated scatter source experimentally (test hypothesis)
(5) Develop a laboratory test method for supplying the data required for the model.

The Missing Link
Examination of error and scatter sources

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Typical propagation of errors analysis - Suppose you have a function

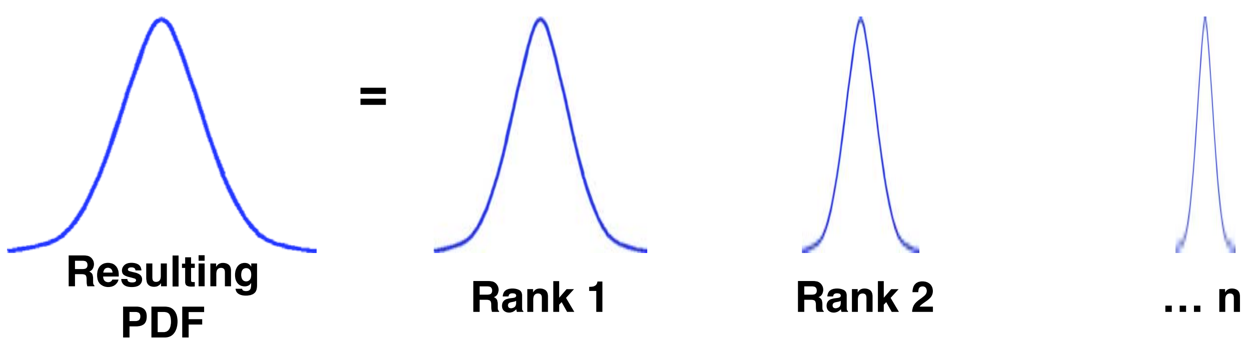
$$P = f(a_1, a_2 \ldots a_n)$$

Then, you can estimate the standard deviation by taking partial derivatives as

$$\sigma_P^2 = \left(\frac{\partial f}{\partial a_1}\right)^2 \sigma_{a_1}^2 + \left(\frac{\partial f}{\partial a_1}\right)^2 \sigma_{a_1}^2 + \sum_n \left(\frac{\partial f}{\partial a_n}\right)^2 \sigma_{a_n}^2$$

$$\sigma_P^2 \cong k_1 \sigma_{a_1}^2 + k_2 \sigma_{a_1}^2 + \sum_n k_n \sigma_{a_n}^2$$

This illustrates why corrosion is difficult to predict. For example, if P is a strong function of a_1, then the small natural variations that occur in a_1 will produce large scatter in P.



What do we need?

"If it were easy, someone else would have done it before now"

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1) Something overlooked previously (hypothesis)
    - Environmental variable
    - Spatially varying (to explain site variability)
    - Temporally varying (to explain behavior of extreme value curves)
    - Strong influence on corrosion
2) Need to accept and use environmental variability (meas., control, predict)
3) Model that enables incorporation of environmental variability
4) Measurement method(s)
    - Prove variable significant
    - Enable quantification
    - Provide data for model
    - Verification

Hypothesis
Water

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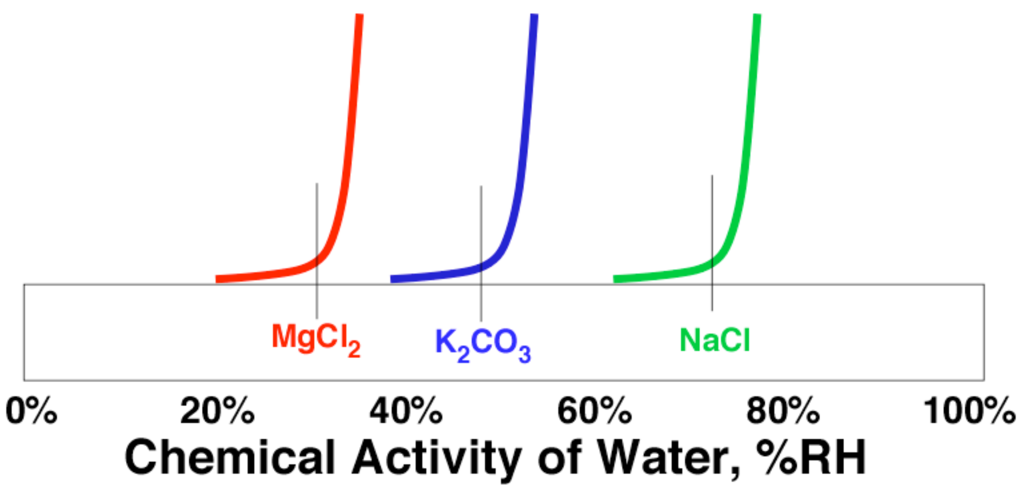
1) Something overlooked previously - No, but considered constant
   - Environmental variable - Certainly, but how much?
   - Spatially varying - Conclusion of NBS study
   - Temporally varying - Annual, seasonal, sunspot
   - Strong influence on corrosion - Yes, but unclear



Hypothesis

The hypothesis is that at the deliquescence point for the salts in a particular environment, the salts against the surface of the pipe become a concentrated liquid and the corrosion rate increases exponentially or otherwise.

The Black Box Approach

Variables Types:

1. Fixed at a given site
2. Vary at any site

How would we use this?

Expected Value of a Function

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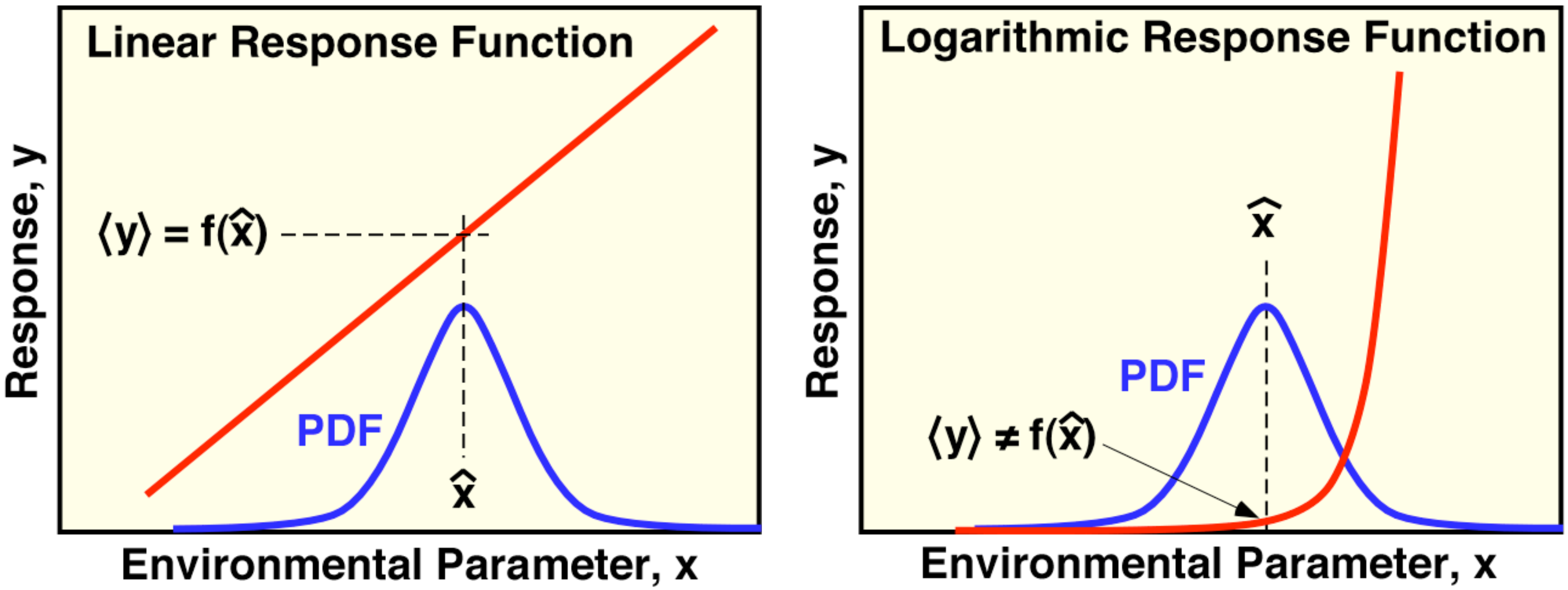
If you have a linear function of a variable, then the expect value is the value for the mean of the input variable.



In the case of a logarithmic function, this may not even be close and the frequency of the occurrence of the extreme may be a better method of estimating the mean. For example, “time of wetness” is frequently used to estimate atmospheric corrosion damage.

An Expected Value Based Model

Examination of error and scatter sources

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The corrosion damage then is just the sum of the corrosion rate multiplied by the time that those specific conditions existed as

$$\langle D \rangle = \sum_{k} R(a_n) F(a_n)$$

This assumes that the corrosion rate adjusts instantly to changing environmental conditions. For a continuous function of one variable this becomes

$$\langle D \rangle = \int R(a_n) F(a_n) da$$

Where F is now a frequency distribution. Rank ordering the variables allows a first order approximation of

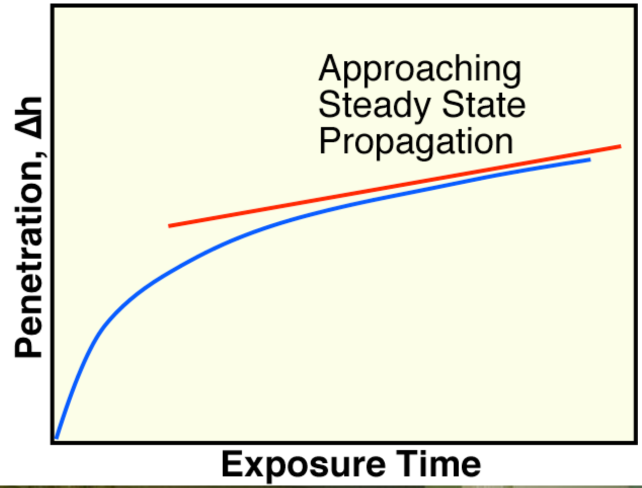
$$R(a_n) \cong R_1(a_1)$$

Where all less significant variables are held at their mean values. Terms would be added as needed to improve predictions

This approach has two great advantages: (1) variables are no longer assumed constant, and (2) varying the frequency distribution allows comparing rates.

Measurement Methods
Examination of error and scatter sources

Proper evaluated requires an *in-situ* measurement technique for obtaining a corrosion rate as a function of exposure conditions as they change.



Steady State Model

Requirements for Measurement Method

The proposed model is a steady state model. This imposes some requirements on the desired measurement method:

1) **Prefer *in-situ* measurements**
   - **Current rate and not an integrated sum of the damage**
   - **Allows for monitoring response to change in variable(s)**
   - **Allows for acquiring data on multiple conditions in a single test**
2) **Electrochemical Method**
   - **Accurate - Measure current not mass**
   - **Quick - Measurements take time, but relatively quick**
   - **Flexible - Numerous sample shapes and geometries can be used**
   - **Cons - Interpretation can be difficult or impossible**

Three different electrochemical techniques are being evaluated for this purpose.

1. **AC impedance (aka. Electrochemical Impedance Spectroscopy EIS)**
2. **Potentiostatic Electrochemical Noise**
3. **Zero Resistance Ammeter Based Electrochemical Noise**

Electrochemical Results

AC Impedance or Electrochemical Impedance Spectroscopy

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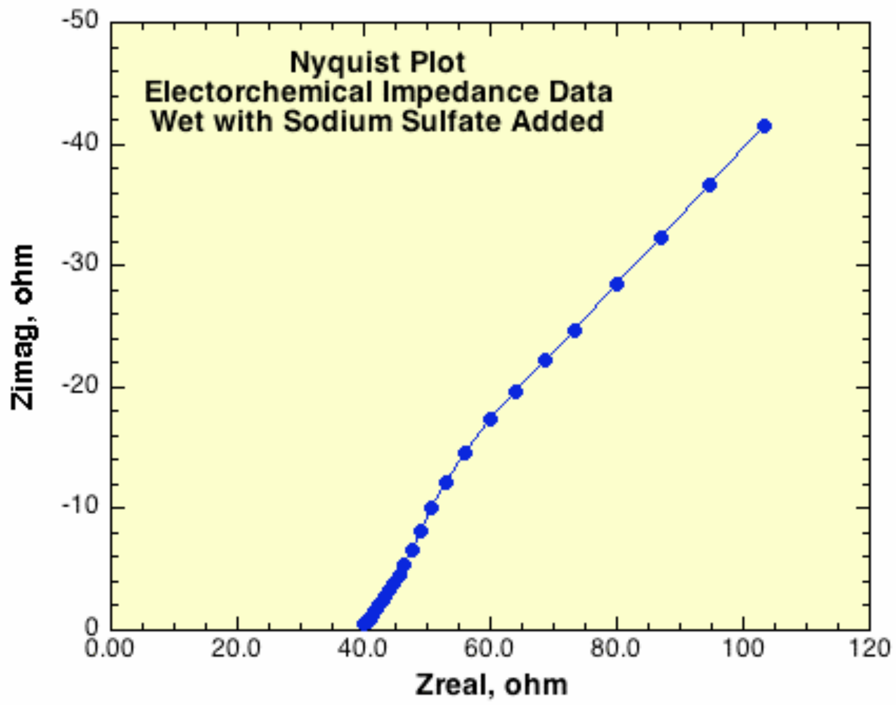

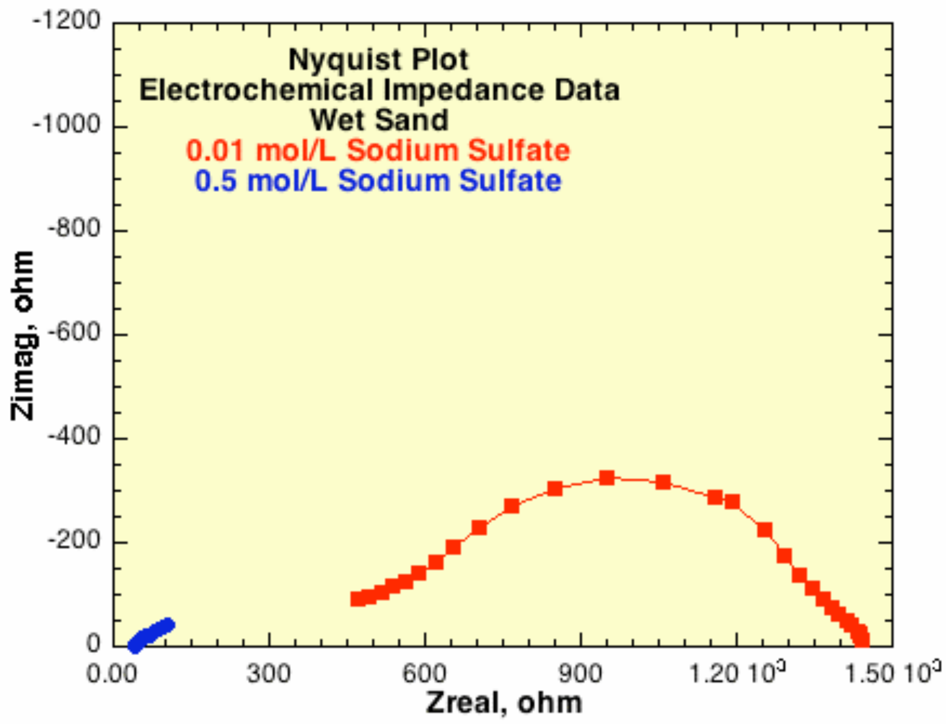

Electrochemical Results

Potentiostatic Electrochemical Noise

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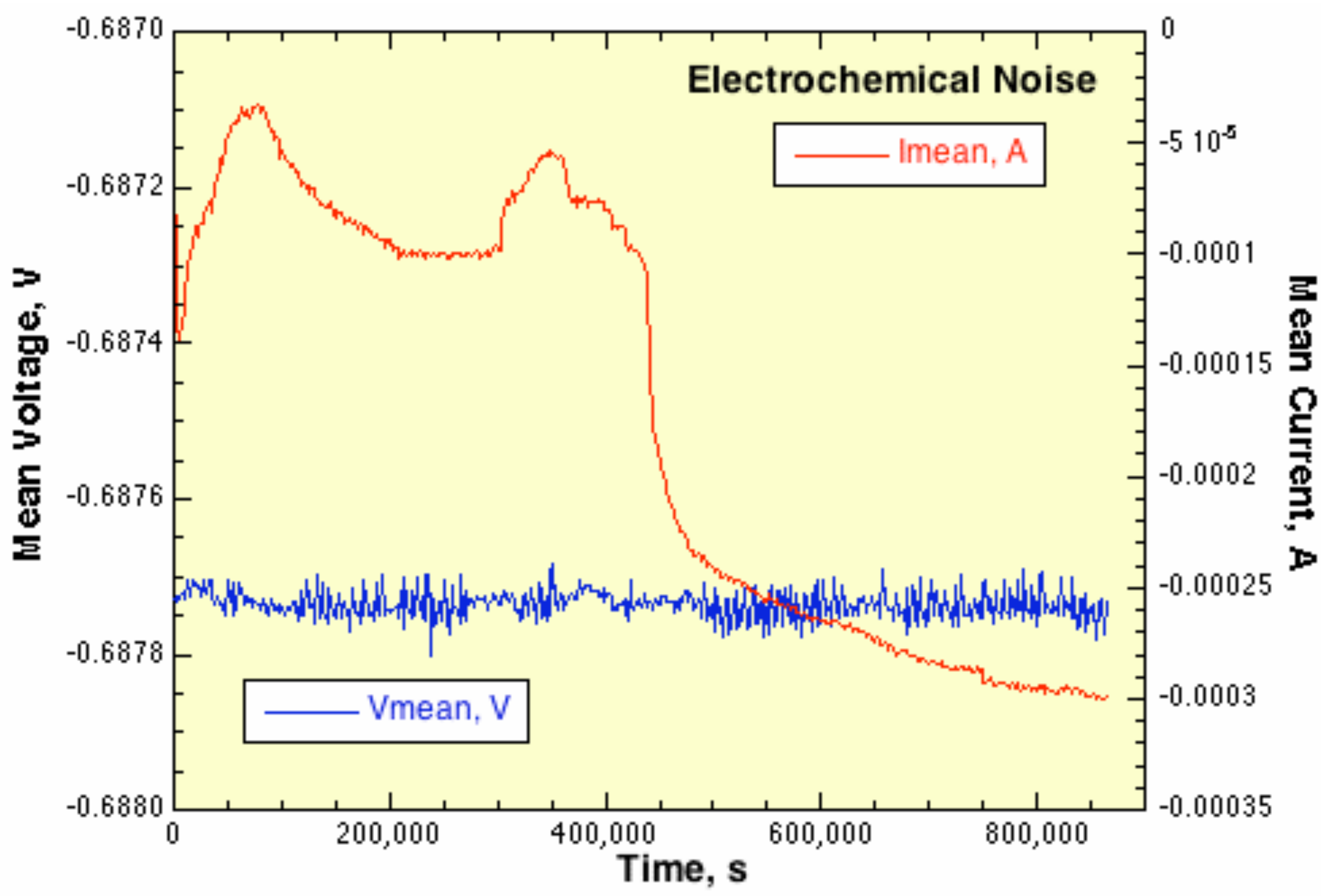

Corrosion Coupons
Examination of corrosion layers on samples

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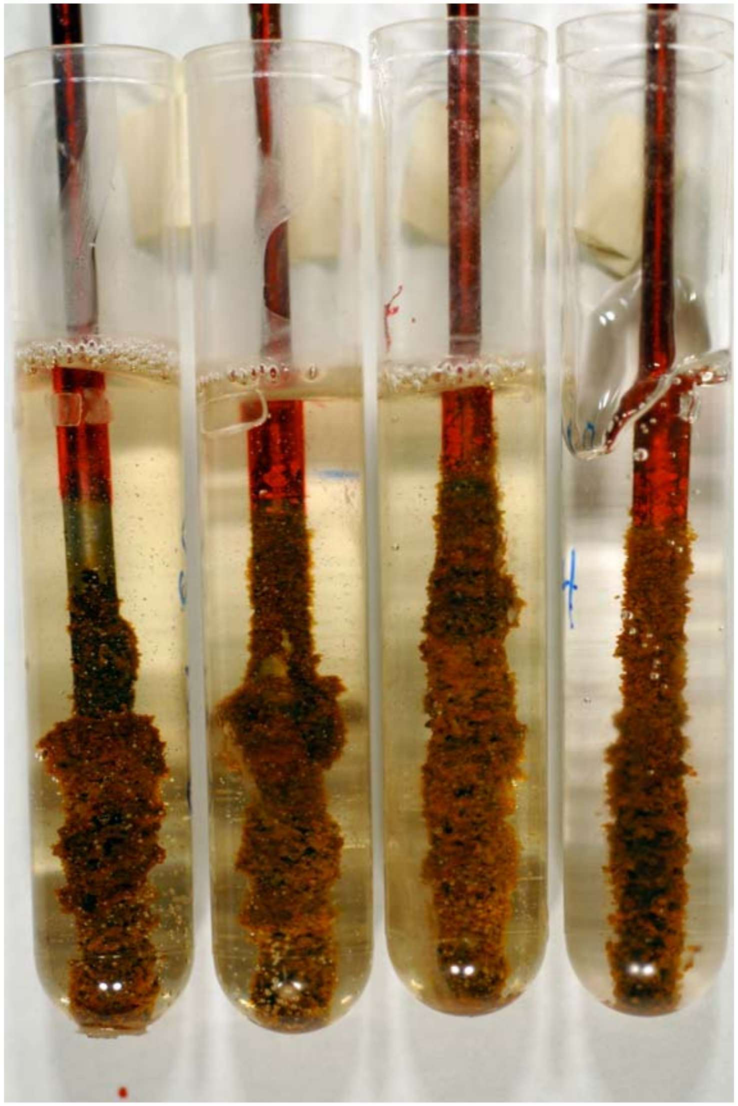
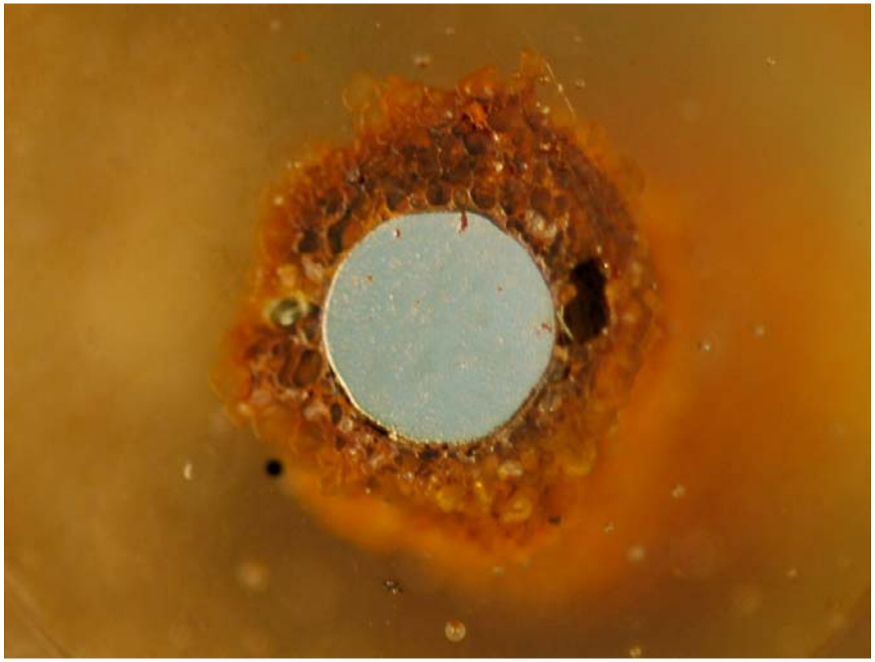


Corrosion Coupons

Examination of corrosion layers on samples



Remaining Issues

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1. A quantative measurement tool that will enable the “black box” semi-empirical approach to the prediction of the influence of a stochastically varying environmental parameters on corrosion rates is still required.

2. Different electrochemical methods and sample geometries may enable in-situ measurement of corrosion rates and variation of important environmental variables and determination of their significance.

3. Breaking variable into those fixed by a site and those that vary at any site simplifies the “semi-empirical modeling through *in-situ* testing. “ However, other variables that can very over time at a given site may need to be considered.

Conclusions

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1. Reexamination of the original NBS studies found that the exposure tests were not well designed for statistical evaluation, but that was 1922.
2. With (1) in mind, the evaluations of the resulting measurements were very thorough and used cutting edge statistics for the time (1935-57).
3. Analysis of the original NBS data did not reveal any new, previously undetected environmental factor that could explain the scatter in the results.
4. The hypothesis that water and surface wetness is important is not new; and in fact, was one of the conclusion of the original NBS studies.
5. A method for "semi-empirical: quantification has been proposed (expected value, ranked variables, add variables to reduce uncertainties, vary frequency distributions to evaluate annual, seasonal, and spatial variations)
6. While extensive measurements have been conducted, the electrochemical data is disappointing. There are indications of the hypothesized trend, but passivity, mass transport, and other factors create uncertainties in the interpretation.
7. While water in contact with the surface is an important variable, it is not the only possibility that a working model may need to include (oxygen, carbon dioxide, soil chemistry, and biological activity may also vary spatially and temporally).

The hope is that, by identifying the more significant sources of variation and dealing with them one at a time in order of significance, a complete model will evolve.